Catalytic Autothermal Reforming

by

Michael Krumpelt, Theodore Krause, John Kopasz

Rolf Wilkenhoener, Shabbir Ahmed

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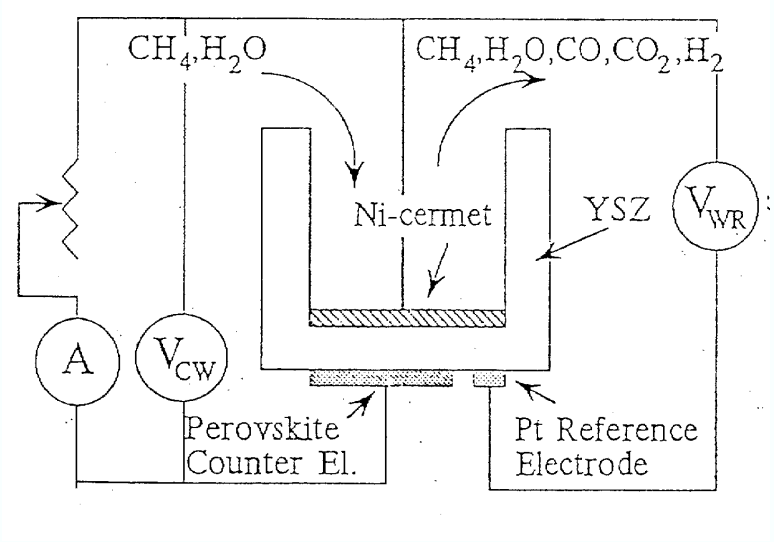
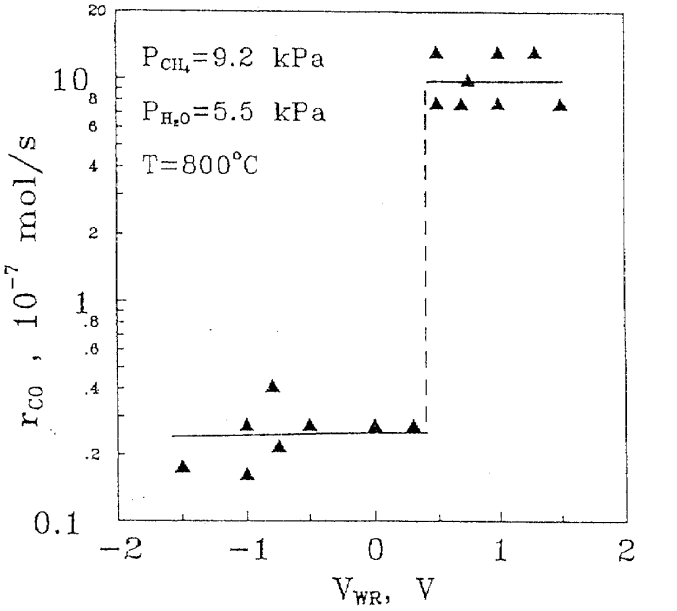
ANL's catalysts are spin-offs of SOFC anodes

- A "non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA)* effect has been observed for metals on oxide ion conducting substrates.



Schematic of the fuel cell reactor



Effect of V_{WR} on the rate of CO formation; Catalyst C4

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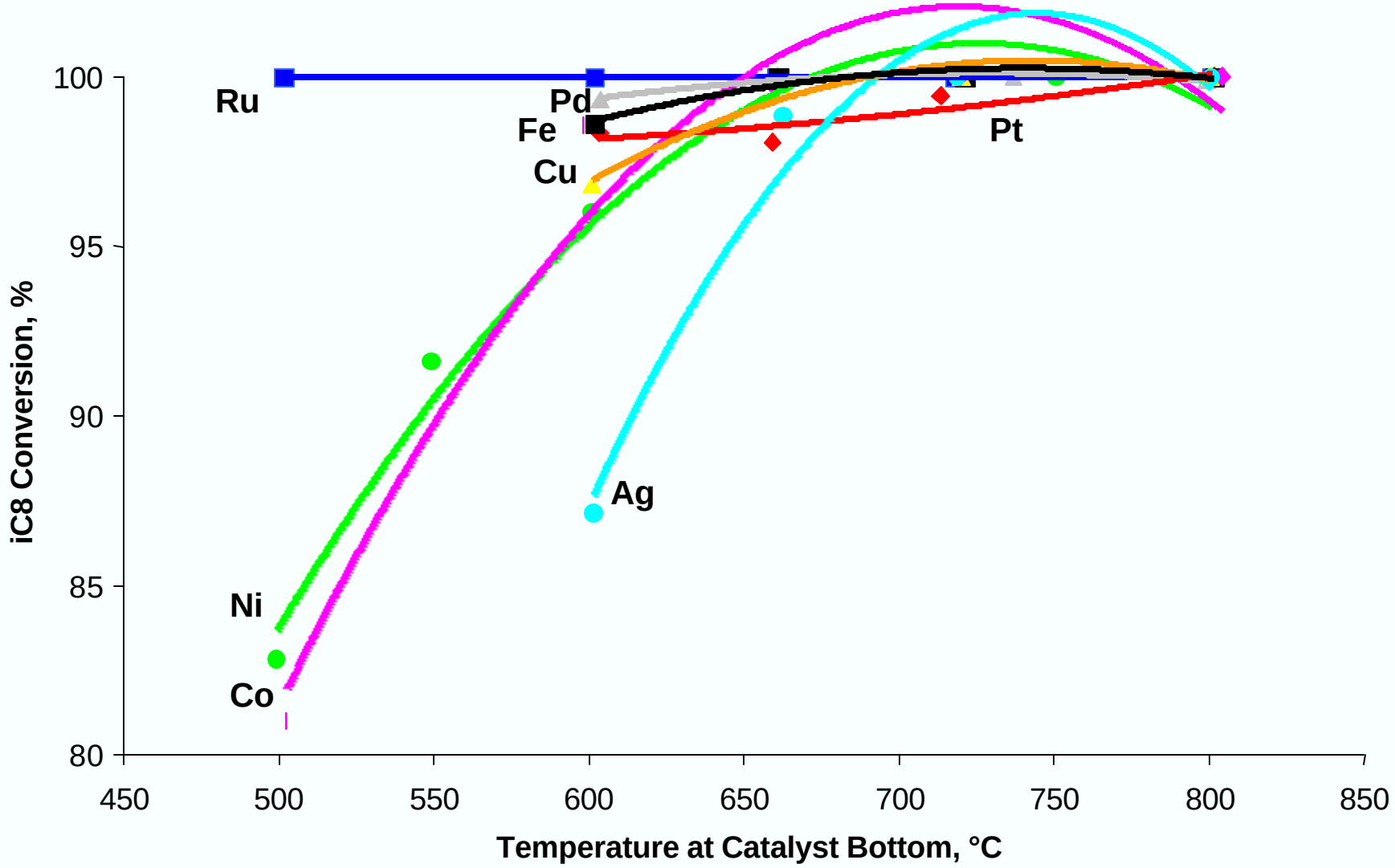
* I.V. Yentekakis, Y. Jiang, S. Neophytides, S. Bebelis and C. G. Vayenas, 2nd European Solid Oxide Forum, Oslo, 1996, p. 131.
C. G. Vayenas, S. Bebelis, Catalysis Today, 51 (1999) 581.

Objectives and Approach

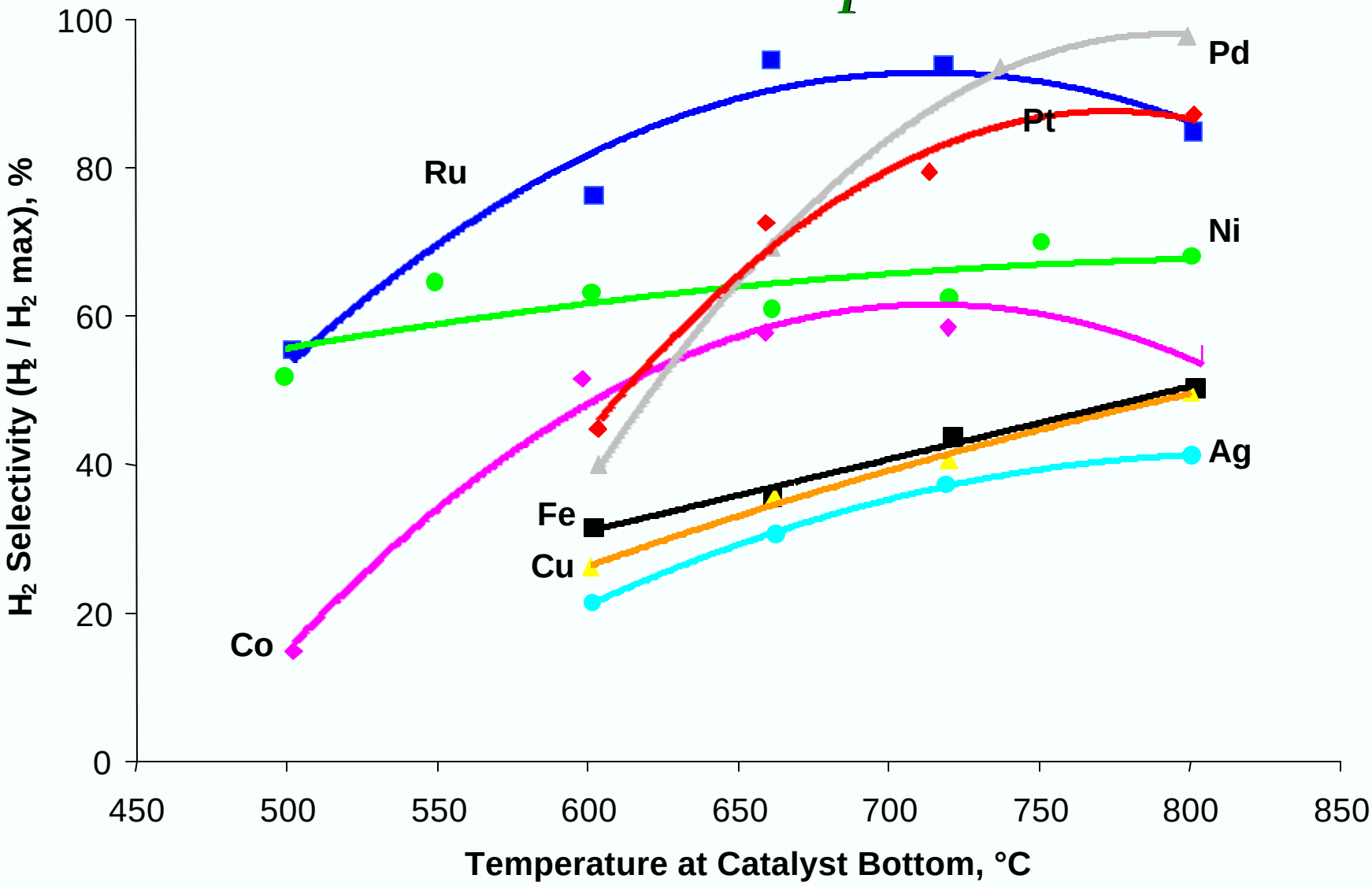
- Improve catalytic activity and reduce cost of ATR catalysts to reduce size of processor and improve start-up time

- Measure hydrocarbon conversion and hydrogen selectivity versus space velocity for various combinations of oxide-ion conductor / metal combinations

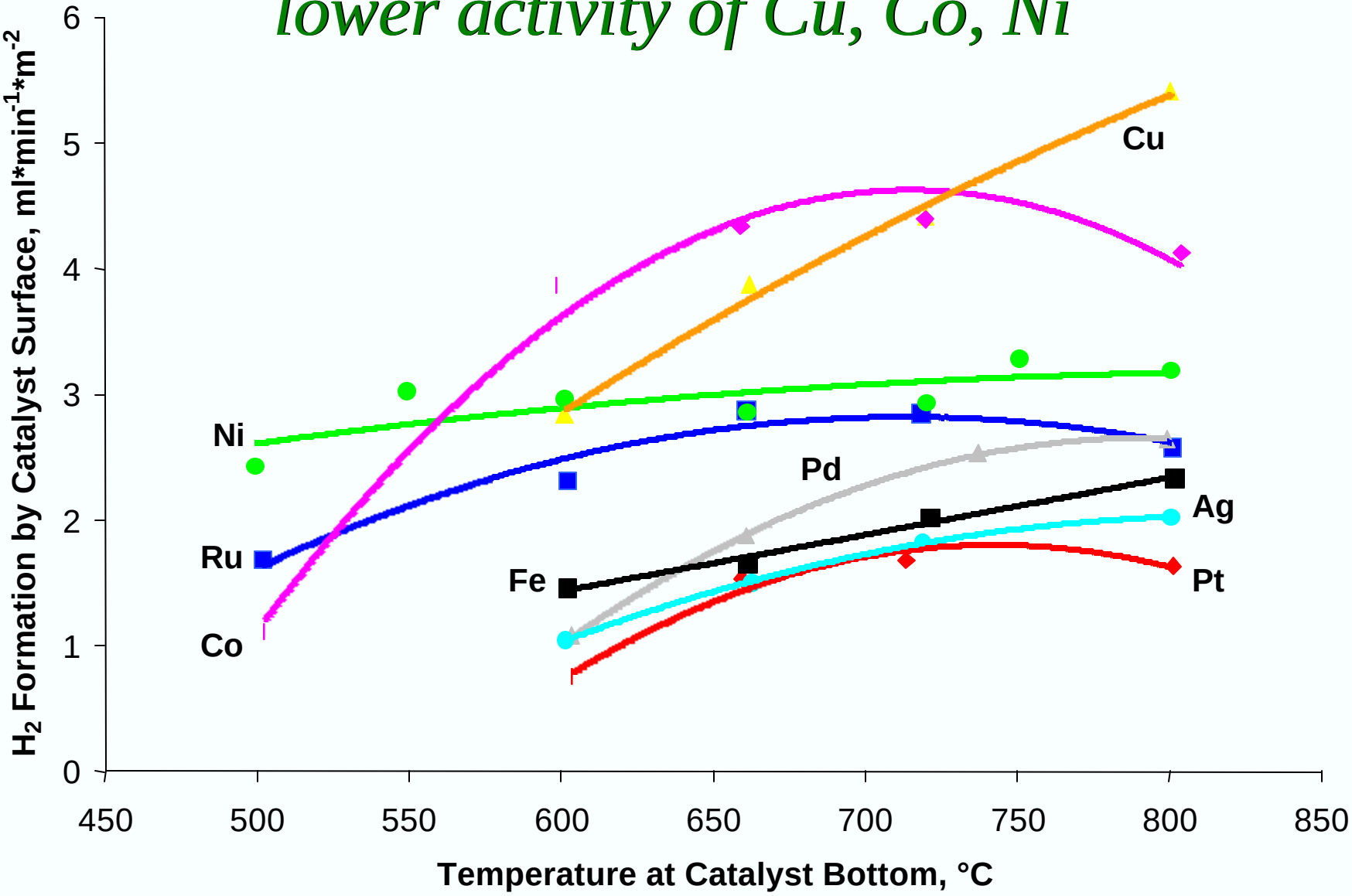
Conversions are close to 100% above 650°C



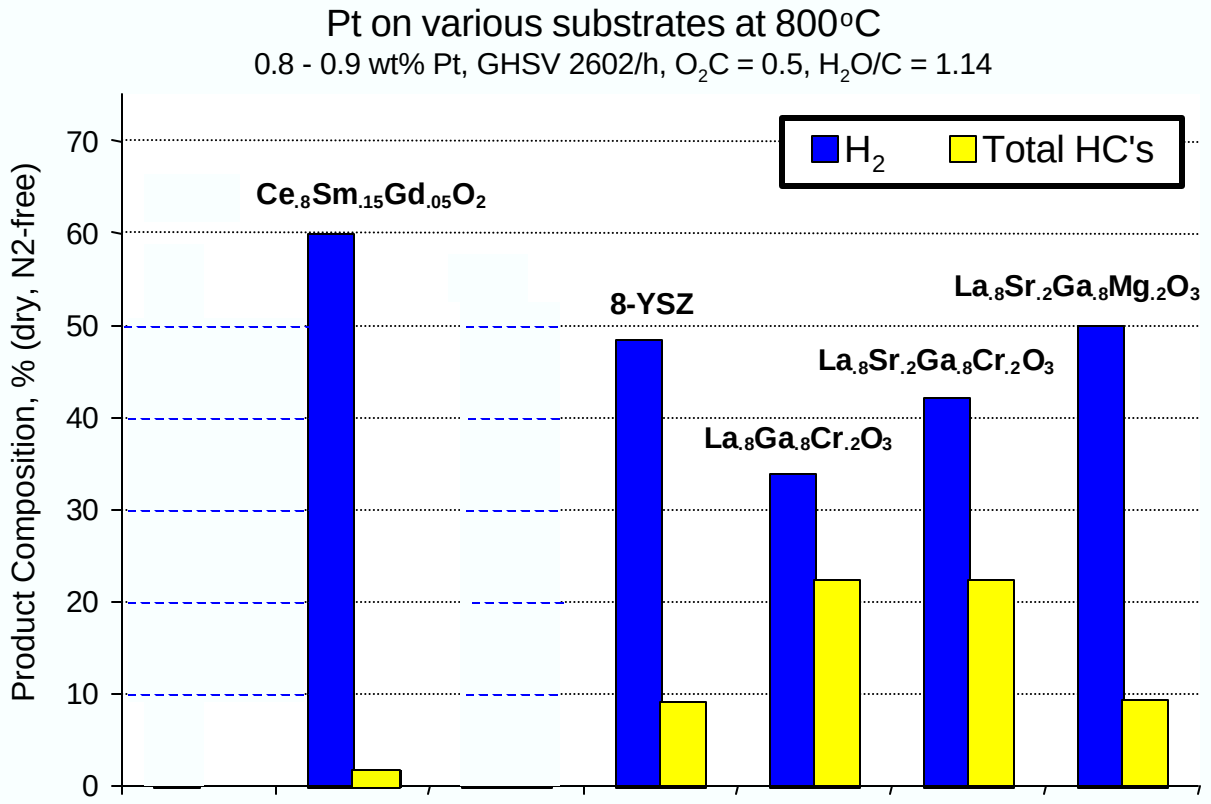
Ruthenium and palladium appear to be more selective than platinum



Differences in surface area may account for lower activity of Cu, Co, Ni

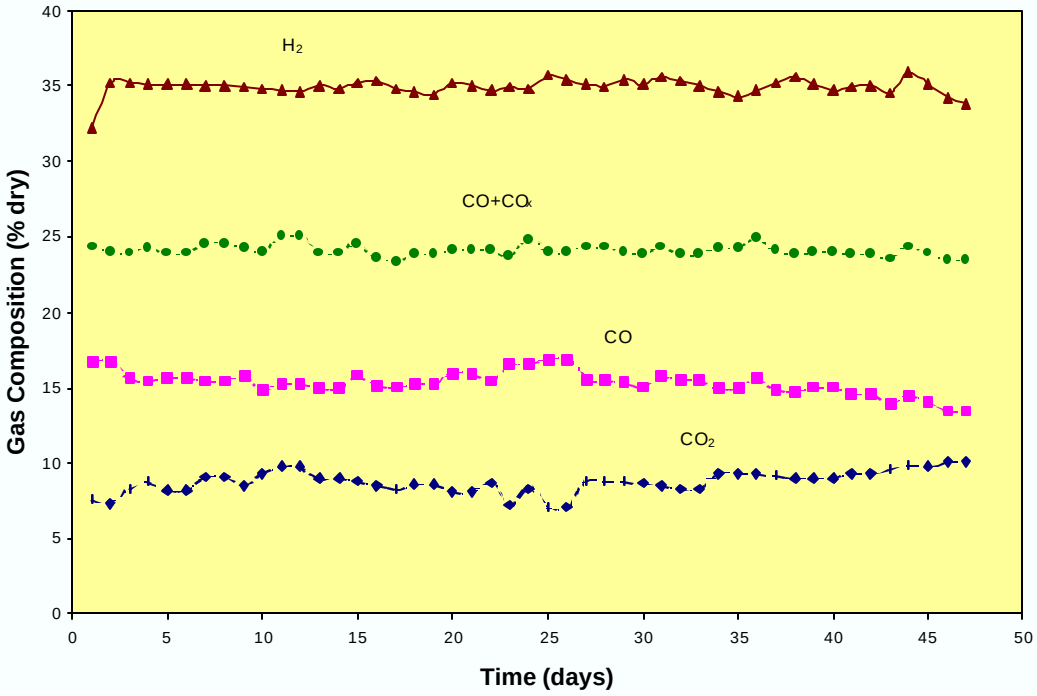


Ceria, zirconia, and lanthanum gallate are Suitable Substrates



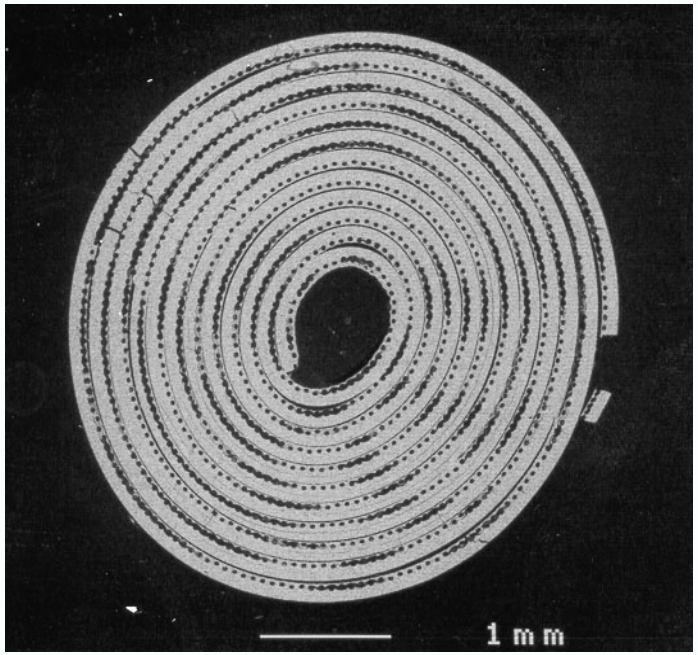
Long term tests with benchmark fuel show little degradation after 1000 h

- Less than 5% decrease in hydrogen output after reforming mixed fuel containing isooctane, methylcyclohexane, pentene, and xylene for 1000h



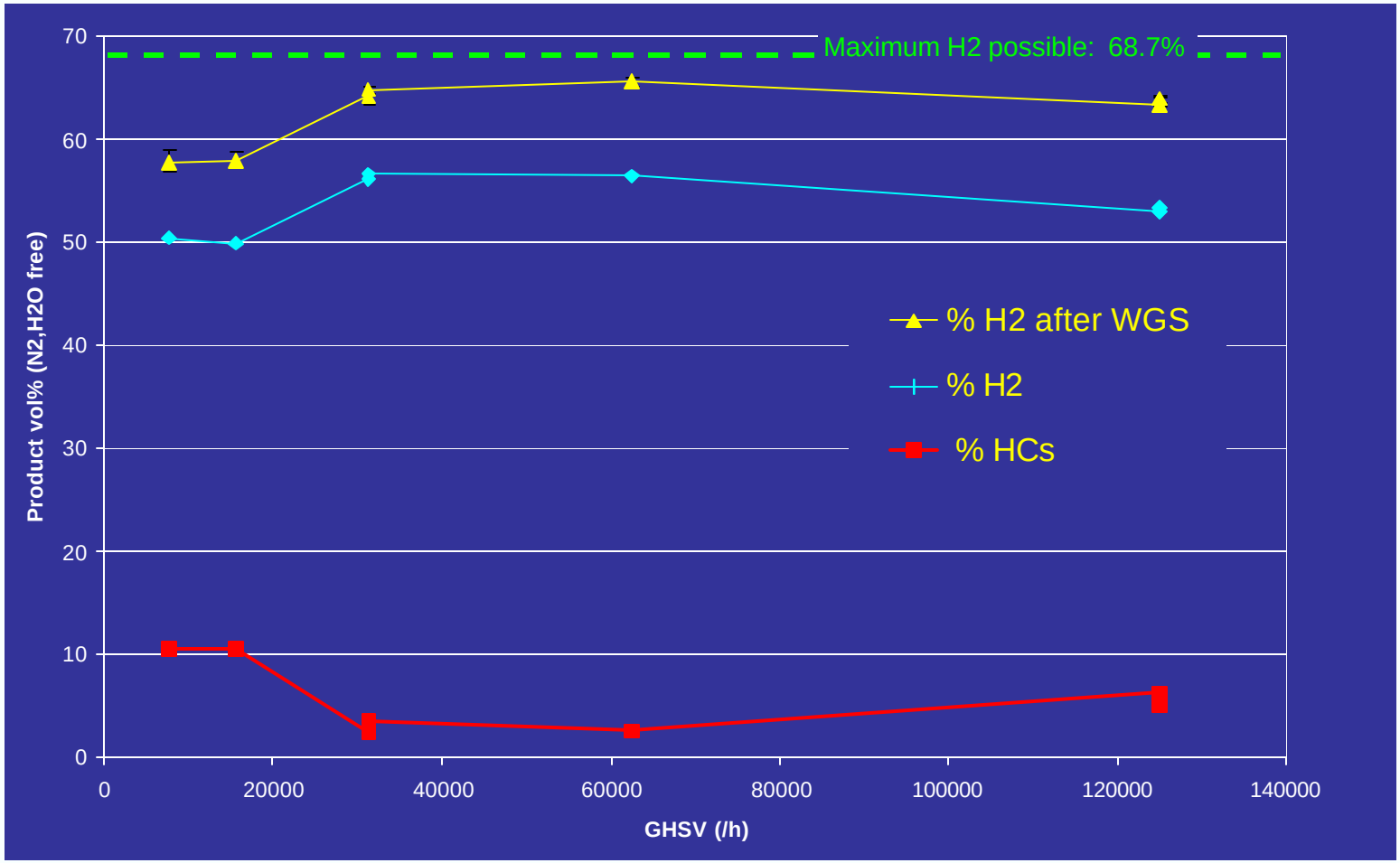
Micro-channel monolithic catalyst allows smaller reactor design

- Diffusion controlled reactions are accelerated
  - Shorter diffusion length
- Lower catalyst loading needed
  - More catalyst exposed to gas
  - Less catalyst is buried
- **Channel Width: 30 μm**
- **Straight through or serpentine channels**

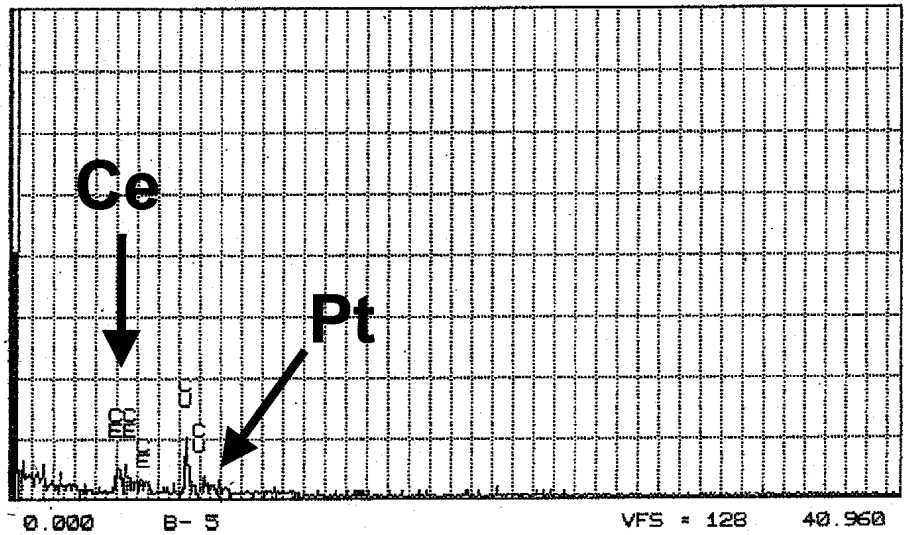


Hydrogen yields from a micro-channel catalyst configuration are maintained at high space velocities

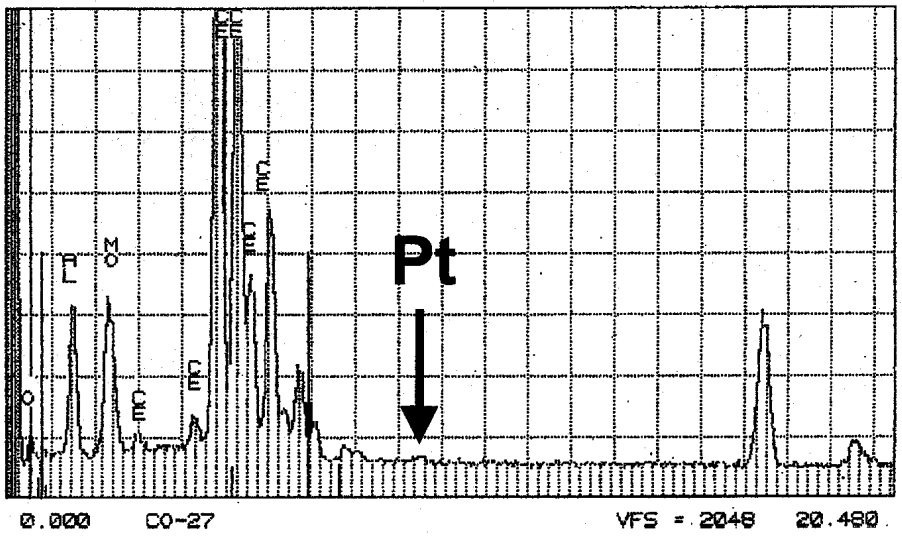
*** Monolith: 1-cm. long, 1-cm. diameter**



TEM-EDAX on KAM 33 Fresh



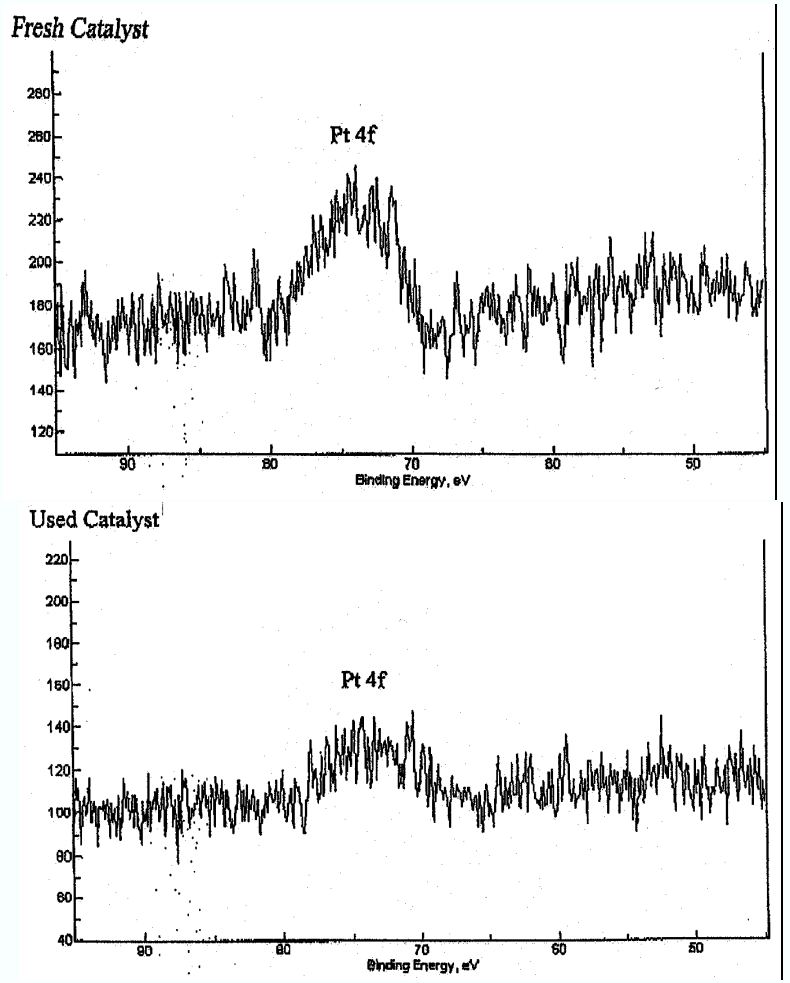
5 s Acquisition



300 s Acquisition

XPS: Pt 4f Scans

It appears that some of the metal disperses over the surface or into the substrate



Observations from Pt EXAFS

	Composition	Particle sizes	Reduction Stability	Comments
TARK-44	Pt/CeO_2	>10 D	High	Pt_4 No Pt-O
TARK-13	Pt/CSAO (prep 1)	< 5 D	High	No Pt-Pt Pt-O-(Ce)
TARK-19	Pt/CSAO (prep 1)	< 5 D	Med.	No Pt-Pt Pt-O-(Ce)
TARK-34	Pt/CGO	< 5 D	Low	No Pt-Pt Pt-O-(Ce)

Relation to Other Catalysts

- Three-way automotive catalysts contain CeO_2 rare earth oxides, and noble metals
  - CeO_2 and rare earth oxides are separate phases
- Lanny Schmidt's catalyst consist of rhodium or platinum on an "inert" alumina surface
- ANL catalysts consist of "active" oxide-ion conducting substrates with transition group elements

Interaction with Industry

- Catalyst formula is being licensed to United Catalysts
- Manufacturing methods will be optimized under a CRADA with United Catalysts
- Samples of catalyst were provided to several industrial organizations for evaluation under confidentiality agreements

Response to Reviewer Comments

- Make more effort to improve catalyst
  - We have and plan to continue
- Include fuel composition as a variable in catalyst development
  - John Kopasz will report results
- Consider cost issues
  - Materials cost is a principal consideration in catalyst optimization
- Investigate effect of residence time on CO formation
  - Good point; we will

Future Plans

- Optimize metal/substrate combination for high activity and low cost
- Optimize micro-channel configuration with or without support structure and address mechanical properties

Project Timeline

May 1995: Started screening for hydrocarbon reforming catalysts

September 1996: Identified new catalyst as the most active for C_8H_{18}

February 1997: Verified catalyst is fuel flexible (pure HCs tested)

April 1997: Demonstrated conversion of gasoline

November 1997: Demonstrated catalyst performance in engineering scale reactor

January 1998: Started correlating formulation with activity

May 1999: Initiate licensing discussions with United Catalysts

February 2000: Reduced cost by an order of magnitude

May 2000: Demonstrated 1000 hour Life

May 2001: Activity versus cost trade-off defined

March 2002: Stability versus manufacturing method defined

September 2002: Optimization complete